Tuning of the electronic screening and electron-phonon coupling in doped SrTiO$_3$ and WO$_3$

T. Jarlborg

DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Genève, Switzerland

The electronic structure and the electronic part of the electron-phonon coupling λ is calculated for doped SrTiO$_3$ and WO$_3$ systems in the perovskite structure. Dilute doping is treated by supercells and the virtual crystal approximation. The long-range part of the coupling is found to be weakly screened for low doping, when the material is close to insulating. The low-q part of λ becomes large despite the low density of states. This is consistent with the appearance of superconductivity for dilute doping.

The traditional explanation of superconductivity relies on a large, attractive electron-phonon coupling λ, which overcomes the Coulomb repulsion between electrons at the Fermi energy E_F.[1] A large λ needs in turn a large density of states (DOS) at E_F, $N(E_F)$, since λ is proportional to $N(E_F)I^2/M\omega^2$, where I is the matrix element for the coupling, M is an atomic mass, and ω a representative phonon frequency.[1] However, superconductivity was observed by Schooley *et al.*[2] in nearly semiconducting materials like in Nb-doped SrTi$_{(1-x)}$Nb$_x$O$_3$ and by Raub *et al.*[3] in Na-diluted tungsten bronze Na$_x$WO$_3$. Superconductivity in such materials is surprising, because $N(E_F)$ is very small for the actual doping concentrations. The Nb (or charge carrier) concentration x, for optimal T_C is of the order 10^{20} cm^{-3}, corresponding to about 0.006 electrons per formula unit (f.u.), making E_F fall in a low-DOS region near the gap. According to theories based on so-called intravalley and intervalley coupling, where attractive interaction via exchange of selected phonons overcomes the Coulomb interaction, it is possible to get superconductivity despite the low DOS.[4] However, the real band structure for SrTiO$_3$ (Ref. 5) is not compatible with the one in the model. A subsequent experimental work found a ''double'' superconducting gap, which was interpreted as a result of a two-band feature of SrTiO$_3$.[6] Recent works on oxygen-deficient WO$_3$ reported superconductivity in twin walls.[7] The superconducting transition temperatures in the above-mentioned systems are not high, 1–3 K, but the discovery of high-T_C superconductivity in other, layered oxides, has led to renewed interest in these materials. The carrier concentration and DOS in high-T_C oxides are not extremely low, but, on the other hand, T_C is very high. Therefore, the problem in these two types of oxides might be related in that a large λ has to be understood in view of a modest DOS, at least if superconductivity is mediated by phonons. Indeed, a recent experimental work suggests a much higher T_C at the surface of Na-doped tungsten bronze.[8] These materials are ideal for studies of the influence of electronic screening on the electron-phonon coupling, since they can be tuned from a semiconductor to a metal by doping. A discussion of the screening mechanism for high-T_C oxides in terms of the dielectric constant, has been given by Weger.[9] There are also arguments for weak screening in high-T_C oxides based on nonadiabatic conditions for low-mobility electrons in normal phonon vibrations,[10] but such assumptions are not appropriate for these systems. Here we contribute to these studies by doing approximate, but parameter-free, nonconstrained, determinations of the electronic structure and the electronic part of the electron-phonon coupling as function of doping for the two systems mentioned above. The calculations focus on λ without detailed discussion of the Coulomb repulsion, superconductivity, or effects that can compete with superconductivity.

The electronic structure is calculated using the self-consistent linear muffin-tin orbital band method in the local-density approximation. So-called full-potential corrections are not included, and the matrix elements for electron-phonon coupling converge actually better than total energies. Therefore the differences in total energies of phonon distortions are not determined. However, bands and DOS are expected to be good for this close-packed structure. The elementary cell of SrTiO$_3$ is simple cubic, perovskite type, with one Sr at the corner, one Ti at the center, and the oxygens at each of the cube faces. The same structure can be applied to the Na$_x$WO$_3$ or O-deficient WO$_3$ systems, when there are no structural distortions.[7] To study doped cases, the unit cell is doubled in each direction, with a total of 40 atoms. In the titanate, one of the eight Ti sites is replaced by Nb, while seven of the eight Na sites in the case of W-bronze are unoccupied. In the virtual crystal approximation, one (or all) of the Ti atoms in the supercell has been assigned an extra, noninteger, charge to account for low doping concentrations. This concerns the electronic as well as the nuclear charge in order to maintain charge neutrality. For the W-bronze, two dopings are considered. In one set of calculations, it is the single Na atom that is given a noninteger charge; in another set it is one of the W sites that plays the role of virtual atom with all Na sites unoccupied. The resulting total DOS functions are calculated by tetrahedron k-space integration. Figure 1 shows the DOS for pure and doped SrTiO$_3$. The band structures are not much different in the virtual crystal cases compared to what is shown in Fig. 1, except that E_F falls closer to the gap edge, corresponding to the case of optimal doping. The gap is about 2.5 eV for the titanate, in fair agreement with early band calculations that were adjusted to agree with optical data.[5] The gap is ''direct'' at the zone center, with a conduction-band minimum at the Γ point. The Fermi surface consists of tiny Γ-centered ''balls'' for very dilute electron doping, which increase in size for larger doping. In the W-bronze the bands and the
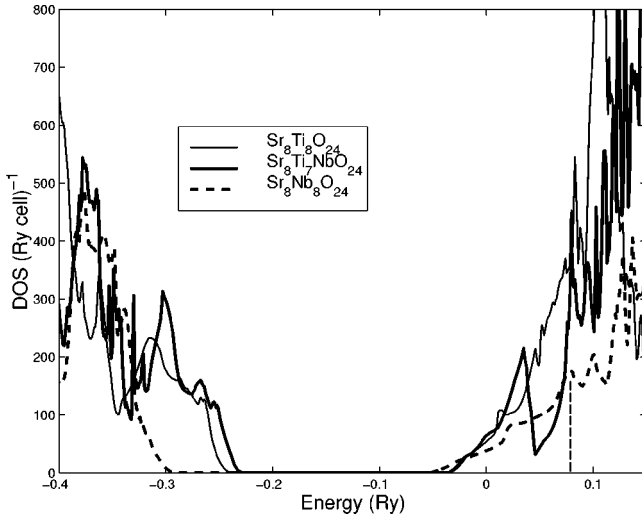
FIG. 1. The DOS of $Sr_8Ti_8O_{24}$, $Sr_8Ti_7NbO_{24}$, and $Sr_8Nb_8O_{24}$ all lined up at a band filling of 193 electron/cell. The Fermi energy is in the gap, at 0, and at the vertical line, respectively.

DOS near the gap are similar to the ones of the titanate, but the gap is smaller, about 1.5 eV.

The total $N(E_F)$ in the doped case $Sr_8Ti_7NbO_{24}$ is 65 (Ry 40-atom-cell)$^{-1}$. The additional Nb takes most of the partial d-DOS, so that each of the seven Ti atoms, and in particular the most distant one from the Nb impurity, has smaller DOS than at the same band filling for the undoped case. The whole system shares the additional charge given by a Nb impurity, much like in a rigid-band metal, a fact that is favorable for the virtual crystal approximation. The observation of superconductivity is for low carrier concentrations, corresponding to about 0.05 electrons in the 40-atom cell. A rigid shift of the DOS puts E_F 8 mRy above the gap edge for this concentration, and the total DOS is about 1.6 states/Ry and elementary cell. This is mostly of Ti d, DOS, but even so this appears low compared to about ten states per Ry and atom in bcc Nb and it would suggest a low λ in $SrTiO_3$.

The value of the total λ is a sum over all possible phonon modes ν.[11] Since the full phonon spectrum is not determined here, we use simplified ''modes'' where the displacement is done for one atom at a time, for totally $\nu=3n$ modes, where n is the number of atoms in the cell. The goal is to study the variation of the electronic screening and λ among systems with different doping, and therefore it is important to consider identical modes in each case. The simplified modes are sufficient for this purpose, but the quantitative values of λ for real, individual phonons are not obtained. The phonon part of λ, the force constant for the averaged real-phonon spectrum, can be taken from experiment in related materials. Although this part is not expected to vary much with the doping, we cannot verify if λ becomes large because of softening of the phonon spectrum. Instead, we investigate the role of electronic screening for an enhancement of the electronic numerator $\eta=NI^2$ of λ. The matrix element $I=\langle\Delta V(r)/u\rangle$, is the integral of the change in potential $[\Delta V(r)]$ due to an atomic displacement u. This matrix element has several terms depending on the number of multipoles of $\Delta V(r)$. The first monopolar term is the screened Madelung shift, which couples electronic states of the same l. The matrix element depends on scattering between k points

$\vec{k}$ and $\vec{k}'$. The small Fermi surface makes $\vec{k}\simeq\vec{k}'$. For the case $\vec{k}=\vec{k}'$ one can simplify the general expression for λ[11] into an approximate form:

$$\lambda_\nu=\frac{\left[\sum_{i,l} N_{i,l}(E_F)I_{i,l}\right]^2}{N(E_F)M_\nu\omega_\nu^2u_\nu^2}, \qquad (1)$$

$$I_{i,l,\nu}=\int R_{i,l}^2(E_F,r)\Delta V_{i,\nu}(r)d^3r. \qquad (2)$$

Here $R_{i,l}$ is the radial wave function for the l state on atom i. $\Delta V_{i,\nu}$ is the change in potential on site i caused by moving atom ν the amplitude u_ν (here 1% of the lattice constant), and it is in general delocalized over several sites. The elastic energy due to the deformation is $M_\nu\omega_\nu^2u_\nu^2$. The total $\lambda=\Sigma\lambda_\nu$ is the sum over all possible (x,y,z) displacements of one atom at the time in the unit cell. The change in potential due to a displacement of a single ion, and the monopolar contribution to η, can be large for ionic systems.[15] Calculations for a few test cases show that the contribution for an O displacement towards Ti (or W) is the largest, compared to a perpendicular displacement or for displacements of other atoms. This is probably because the large ionicity of O is in combination with a short Ti-O distance. Self-consistent calculations with and without the atomic displacement are needed in order to determine the monopolar term, which makes the calculations quite demanding in computing power. In order to reduce the computational task, it is assumed that the results for displacements of equivalent sites in the unit cell are the same because of symmetry, although the symmetry is not perfect because of the additional impurity site.

The next, dipolar term is because of a change in potential of symmetry $l=1$, which can be viewed as the first term due to nonspherical potential effects. Contrary to the monopole term it is localized closer to the moved site, which can be understood from the faster convergence of real-space lattice sums of high-l multipoles. Terms of higher multipoles are therefore not very sensitive to variations of the long-range screening, and thus they can hardly be enhanced for the same reason as the monopolar term. Here we calculate the dipolar term in the rigid muffin-tin approximation (RMTA).[12] The matrix element is due to the rigid displacement of a potential, and in a compound it can be calculated for each site separately.[13] It leads to dipolar coupling, i.e., the l-quantum number of contributing states has to differ by one unit, and the calculated value follows fairly well the total DOS in these systems. RMTA calculations give a good account of λ in nonionic metals.[14] However, in these ionic materials with rather pure, unhybridized l DOS, the dipolar coupling is much smaller than the monopolar one, at least for the lowest dopings. The calculated RMTA value is relatively important only for a good metal like $SrNbO_3$, where the calculated value has its maximum, 3 eV/Å^2, for the case with the highest DOS for the titanates (cf. also Fig. 1 and Table I). The selection rule and the localization of the dipole term make it likely that it will remain small compared to the monopole term even if the RMTA is corrected for self-consistent relaxation. Higher multipoles are neglected.

TABLE I. Calculated η in units of eV/Å^2, and $N(E_F)$ in (Ry f.u.)$^{-1}$ for two dopings of SrTi$_{1-x}$Nb$_x$O$_3$. The small-q values refer to the displacement of O modes in the 40-atom cell and the large q to the displacements in the five-atom cell. The dipolar value is calculated within RMTA.

x (electrons/f.u.)	$N(E_F)$	η (small q)	η (large q)	η (dipolar)
0.01	1.9	22	≤ 0.1	0.1
0.125	8.2	2.5	0.1	2

A displacement of an atom in the enlarged cell is a perturbation, which leads to different charge redistributions for different doping. Interatomic charge transfer between near neighbors is possible even in an insulator, because of hybridization and orbital tails. Over larger distances a metal is a different case because states at E_F help the exchange of charges between all sites. This serves to screen the effect of the perturbation, so more distant sites will not be affected by the perturbation. A long-distance screening is missing for a near insulator at low doping, and the change in potential ΔV reaches further out. Thus, the matrix element I of the monopolar electron-phonon coupling is expected to be largest for the smallest x, and the actual calculations confirm this.

The results are summarized in Figs. 2 and 3. A number of tests are made in order to verify that a reliable trend for $\eta(x)$ can be extracted from the results, despite the statistical fluctuation among individual η values. The quantitative results for a given doping are sensitive to number of k points, distortion amplitude, and to particular conditions of the DOS, but these uncertainties are proportional to the total η value for each case and do not affect the conclusion about the doping dependence. Using the $N(E_F)$ values in Eq. (1) from undistorted or distorted structures, can in a few cases, make a difference by a factor of 2 in the value of η. The results in the figures are the averaged values. It is important to note
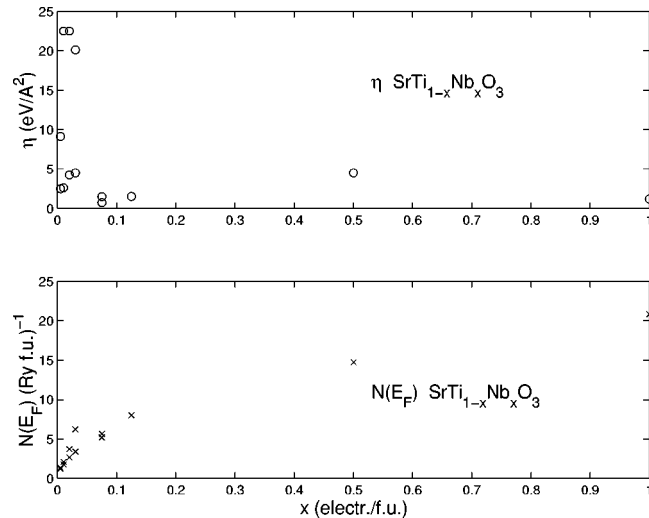

FIG. 2. Calculated η due to O displacements (upper panel) and total DOS at E_F (lower panel) as function of doping x per formula unit of doped SrTi$_{1-x}$Nb$_x$O$_3$. At low doping ($x<0.125$) there are two virtual crystal values for the same doping. The largest values are obtained when the additional charge is concentrated on one Ti site.
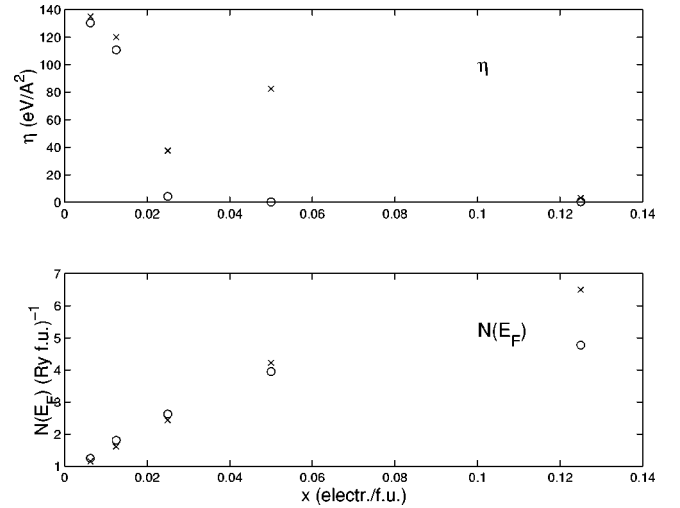

FIG. 3. Calculated η (upper panel) for O displacements and DOS at E_F (lower panel) as a function of doping x per formula unit of Na$_x$WO$_3$ (crosses) and W$_{1-x}$Re$_x$O$_3$ (circles). All values, except the ones for $x=0.125$, are calculated within the virtual crystal approximation.

that there is an amplitude dependence of λ. Distortions in complex, multisite, and multiband systems, can bring (or remove) new bands near to E_F, to make discontinuities in $N(E_F)$ as the displacement amplitude changes. Such nonlinear effects can be very strong in high-T_C oxides.[10] These calculations use 64 k points in 1/8 of the Brillouin zone. First calculations using 27 k points give the same general trends, despite more "scattering" among the enhancement values. But the enhancements at low x appear stronger when using 64 k points. The various systems, with different dopants and different local DOS, all show enhanced $\eta(x)$ for small x for O displacements. The calculations for displacements of other sites are not as complete as for O displacements, but for the considered cases, there are relatively small η, especially for Sr. The variation with doping is smaller, and no evident enhancement at low doping is seen for Sr displacements.

The electronic part of λ [Eq. (1) with the force constant $M_\nu \omega_\nu^2 = 1$] and the total $N(E_F)$ show opposite trends as function of doping, as can be seen in Fig. 2 for the SrTiO$_3$ system and in Fig. 3 for the WO$_3$ system. The coupling is seen to be largest for the near insulators, while the total DOS is largest for the best metals. For cases with equal total doping in the virtual crystal calculations for the titanates, the η values are larger when the doping charge is concentrated on one impurity instead of being spread over several sites. This is because the DOS is enhanced at a single impurity. The total DOS is larger, and as was noted above, the DOS far from a single impurity tends to vanish. The material tends to be insulating between the impurities, which will hamper the long-range screening.

The large monopolar η for some displacements concerns low-q phonon modes, because the screening is weakened only over long distances. By doing the displacements within the elementary five-atom unit cell, one finds only a very small η, independent of doping, as is shown in Table I. Thus, there is a division between a low η for large q and a large, nonscreened η for intermediate q. From the size of the two unit cells considered here, one can situate this division for q

between approximately 0.8 and 0.4 Å^{-1}. In the absense of physical arguments for a reactivated screening over even larger distances, one expects that a large η persists for the smallest q. At large q, near the zone boundary, one expects metallic screening for all dopings, without enhancement of the monopolar η.

The stability of this mechanism for λ enhancement will be delicate at extremely low doping concentration, when the DOS at E_F tends to zero, either totally or locally between impurity sites. The requirement of a uniform distribution of the impurities becomes essential, since no dopant is perfectly itinerant, but the additional charge is always more or less localized around the impurity. Such extreme cases are difficult even computationally, since the interaction between impurities is in the calculation limited by the size of the unit cell. The calculated enhancements for the $SrTiO_3$ system are largest not for the lowest doping, but near 0.01–0.015 electrons/f.u., while for the WO_3 system the largest values were found for the lowest doping.

The results for the two types of materials are similar, with a tendency for having the largest η in the WO_3 system. This is consistent with the experimental situation for superconducting T_C, but the difference appears too small to understand the very large observed T_C in the WO_3 system.[8] These calculations show the trend for one long and one short q value, and do not map out the complete q dependence of the η enhancement, which may be different in the two systems. However, one argument suggests that the screening is indeed better in the titanate system for equal electron doping, which provides an explanation to why the bronze system should have the largest η: The Sr-site in the WO_3 bronzes is essentially unoccupied (only partially occupied by Na) and therefore void of electrons. Electron transport and orbital hybridization, which in the titanate can be done across these sites, are in the bronzes limited to the ''jungle-gym'' cage structure made up of the WO_3 network. This difference should be present even at large q, because the difference in real space concerns part of the near-neighbor interactions. Another difference (which is not investigated here) is that quite different phonon modes are generated by Ti and W atoms, because of their different masses.

In conclusion, we find that the absense of long-range screening in nearly insulating cases for low doping concentrations, is able to enhance λ for long-wavelength phonon modes. This concerns the monopole term, while the dipole term is much smaller. A force constant of a typical amplitude around 10 eV/Å^2 would make λ very large (>10 in the WO_3 system) for special low-q modes, consistent with superconductivity. However, one can also argue that a large λ is favorable to lattice instabilities, and when $\vec{q}$ is small even to stripes.[16] This is in contrast to features depending on short-range interactions, like polarons, which should not be stabilized by this mechanism. An enhancement of the Coulomb repulsion is also unlikely for a mechanism that only affects long-distance interactions. The screening of a collective charge redistribution around an ionic displacement depends on the existence (and shape) of a Fermi Surface (FS), which here is shown to be inefficient over large distances. But the direct Coulomb interaction between two electrons is a property of the electron gas, independent of the FS, and that screening is completed already at small distances, comparable to the electron gas parameter r_s. Therefore, even if a microscopic calculation of the superconducting T_C is missing so far, one can expect that the enhancement of λ for small $\vec{q}$ will dominate effects that prevent superconductivity. According to the results, it should be possible to optimize the enhancement by choosing between localized and itinerant dopants, and by choosing a system with limited neighbor interaction. It is often argued that electronic screening, expressed in terms of a dielectric constant, plays a crucial role for λ enhancements,[9] but this work is, to our knowledge, the first one where this is demonstrated by electronic structure calculations. An example is found where a low value of $N(E_F)$ turns out to be favorable for a large λ and therefore probably also for superconductivity.

[1] J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. **106**, 162 (1957); W.L. McMillan, *ibid.* **167**, 331 (1968).

[2] J.F. Schooley, W.R. Hosler, and M.L. Cohen, Phys. Rev. Lett. **12**, 474 (1964).

[3] Ch. J. Raub *et al.*, Phys. Rev. Lett. **13**, 1352 (1964).

[4] M.L. Cohen, Phys. Rev. **134**, A511 (1964); C.S. Koonce *et al.*, Phys. Rev. **163**, 380 (1967); J. Appel, *ibid.* **180**, 508 (1969).

[5] L.F. Mattheiss, Phys. Rev. B **6**, 4718 (1972).

[6] G. Binnig *et al.*, Phys. Rev. Lett. **45**, 1352 (1980).

[7] A. Aird and E.K.H. Salje, J. Phys.: Condens. Matter **10**, L377 (1998); A. Aird *et al.*, *ibid.* **10**, L569 (1998).

[8] S. Reich and Y. Tsabba, Eur. Phys. J. B **9**, 1 (1999).

[9] M. Weger, J. Low Temp. Phys. **95**, 131 (1994), and references therein.

[10] G. Santi and T. Jarlborg, J. Phys. Chem. Solids **59**, 2121 (1998).

[11] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).

[12] G.D. Gaspari and B.L. Gyorffy, Phys. Rev. Lett. **28**, 801 (1972).

[13] M. Dacorogna *et al.*, J. Low Temp. Phys. **57**, 629 (1984).

[14] D.A. Papaconstantopoulos *et al.*, Phys. Rev. B **15**, 4221 (1977).

[15] T. Jarlborg, Helv. Phys. Acta **61**, 421 (1988).

[16] A. Bianconi *et al.*, Phys. Rev. Lett. **76**, 3412 (1996).